Research Article

Towards the Equation of State for Neutral (C_2H_4), Polar (H_2O), and Ionic ($[bmim][BF_4]$, $[bmim][PF_6]$, $[pmmim][Tf_2N]$) Liquids

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Despite considerable effort of experimentalists no reliable vapor-liquid coexistence at very small pressures and liquid-solid coexistence at high pressures have been until now observed in the working range of temperature $290 < T/K < 350$ for ionic liquids. The measurements of high-pressure properties in low-temperature stable liquid are relatively scarce while the strong influence of their consistency on the phase equilibrium prediction is obvious. In this work we discuss the applicability of fluctuational-thermodynamic methodology and respective equation of state to correlate the properties of any (neutral, polar, ionic) liquids since our ultimate goal is the simple reference predictive model to describe vapor-liquid, liquid-liquid, and liquid-solid equilibria of mixtures containing above components. It is shown that the inconsistencies among existing volumetric measurements and the strong dependence of the mechanical and, especially, caloric derived properties on the shape of the functions chosen to fit the experimental data can be resolved in the framework of fluctuational-thermodynamic equation of state. To illustrate its results the comparison with the known experimental data for $[bmim][BF_4]$ and $[bmim][PF_6]$ as well as with the lattice-fluid equation of state and the methodology of thermodynamic integration is represented. It corroborates the thermodynamic consistency of predictions and excellent correlation of derived properties over the wide range of pressures $0 < P/MPa < 200$.

1. Introduction

Behavior of low-melting organic salts or ionic liquids (ILs) [1–6] in the region of phase transitions is qualitatively similar to that either for high-temperature nonorganic molten salts or long-hydrocarbon-chain organic solvents and, even, for polymer systems. Such characteristic features as negligible vapor pressure $P_\sigma(T)$, undefined critical parameters P_c , ρ_c , T_c for vapor-liquid (v, l)-transition, split of liquid-solid (l, s)-boundary onto melting $P_m(T)$ and freezing $P_f(T)$ branches, existence of glassy states make the problem of metastability to be quite complex but vital for many potential uses of ILs. In particular, thermodynamic modeling and computer simulation of the phase behavior in mixtures formed by ILs with water and low-molecular organic solvents such as ethylene can be of great importance for the further tuning of their operational parameters. If one proceeds from a pure to a mixed fluid, it is especially advantageous to develop the same

format of reference pair potential (RPP) for each component and mixture.

As a first step toward consistent modeling of the phase behavior of IL and its solution we demonstrate in this work how the fluctuational-thermodynamic (FT) EOS [7–12] and the relevant finite-range Len-nard-Jones (LJ) RPP can be applied to model the underlying structure and properties of low-molecular (C_2H_4 , H_2O) and imidazolium-based (1-butyl-3-methylimidazolium tetrafluoroborate ($[bmim][BF_4]$), 1-butyl-3-methylimidazolium hexafluorophosphate ($[bmim][PF_6]$), 2,3-dimethyl-1-propylimidazolium bis(trifluoromethylsulfonyl)imide ($[pmmim][Tf_2N]$)) solvents. For any pure component FT-model is based either on the measurable coexistence-curve input data $P_\sigma(T)$, $\rho_v(T)$, $\rho_l(T)$ (if they are achievable as for C_2H_4 and H_2O) or on the also measurable one-phase density of liquid at atmospheric pressure ρ ($P_0 \approx 0.1$ MPa, T) for ILs. This methodology becomes purely predictive for density $\rho(P, T)$ in any one-phase v, l, s -regions including

their metastable extensions. Only the measurable isobaric heat capacity data $C_p(P_0, T)$ have to be added to the set of input data for prediction of other caloric properties (isochoric heat capacity $C_v(P, T)$, speed of sound $W(P, T)$, and Gruneisen parameter $\text{Gr}(P, T)$) at higher pressures $P > P_0$ and lower $T < T_m$ or higher $T > T_b$ temperatures where T_b is the hypothesized normal boiling temperature $T_b(P_0)$. Its existence itself is a debatable question because the thermal decomposition T_d may be former $T_d < T_b$.

Such approach was proposed recently [7, 8] to reconstruct the hypothetical (v, l) -diagram of any ILs in its stable and metastable regions on the base of only standard reference data on density $\rho(T)$ at P_0 [1–4] and one free parameter, an a priori unknown value of the excluded volume b_0 . To our knowledge this is first attempt to predict simultaneously the whole set of one-phase and two-phase properties for ILs *without the fit at any other pressures including the negative ones*. It was argued that the particular low-temperature variant of the most general FT-EOS [9–12] should be used to obtain the consistent prediction of volumetric properties and the standard response functions α_p , β_T , $\gamma_p = \alpha_p/\beta_T$ by the following equations:

$$P = \frac{\rho RT}{1 - b_0 \rho} - a(T) \rho^2, \quad (1)$$

$$\beta_T = \frac{(1 - b_0 \rho)^2}{2P(1 - b_0 \rho)^2 + \rho RT(2b_0 \rho - 1)} > 0, \quad (2)$$

$$\alpha_p = \frac{(1 - b_0 \rho) [\rho R - \rho^2 (1 - b_0 \rho) da/dT]}{2P(1 - b_0 \rho)^2 + \rho RT(2b_0 \rho - 1)}, \quad (3)$$

$$\gamma_p = \frac{\rho R - \rho^2 (1 - b_0 \rho) da/dT}{(1 - b_0 \rho)}, \quad (4)$$

where b_0 is the excluded molecular volume and $a(T)$ is the T -dependent effective cohesive energy. The derivative da/dT affects the thermal expansion α_p and the thermal-pressure coefficient γ_p while the isothermal compressibility β_T depends only on b_0 -value at the given pressure. The changeable sign of two thermal derivatives α_p , γ_p offers a possibility to predict the properties of anomalous low-temperature substances (such as water, for example) too [7, 8].

Fortunately we have obtained now [13–19] a possibility to test our predictions not only by the direct experimental one-phase data [14, 16, 18, 19] on $\rho(P, T)$ - and $W(P, T)$ -surfaces. Another possibility is offered by comparison of the predictions obtained by FT-EOS for the critical parameters of ILs ([bmim][BF₄]: $T_c = 962,3$ K, $P_c = 3503,9$ kPa, $\rho_c = 438,565$ kg·m⁻³ with those predicted here by the Sanchez-Lacombe EOS for lattice fluid (LF) [15]: $T_c = 885,01$ K, $P_c = 2829$ kPa, $\rho_c = 248,565$ kg·m⁻³ as well as with those simulated by GEMC-methodology [6]: $T_c = 1252$ K, $P_c = 390$ kPa, $\rho_c = 181$ kg·m⁻³. It seems that the relatively close location of (T_c, P_c) -parameters predicted by both EOSs is some guarantee of their reliability while T_c and P_c from [6] are significantly overestimated and underestimated, respectively. Interestingly, the known descriptive factor of compressibility

$r_t = P_c/(\rho_c RT_c)$ estimated by Guggenheim [20] in the vicinity of triple point T_t for argon as $r_t = 0,108$ is equal to close values $r_t = 0,082$ for FT-EOS and $r_t = 0,072$ for LF-EOS but only to very small value $r_t = 0,007$ for result of GEMC-simulations if the common realistic estimate (see below) $\rho_t \approx \rho_l = 5,350646$ mol·dm⁻³ at $T = 290$ K is used. Moreover, it will be shown that the characteristic dimensional parameters P_c^* , T_c^* , ρ_c^* and another compressibility factor $r_c^* = P_c^*/(\rho_c^* RT_c^*)$ obtained by Machida et al. [14] by the fit to (P, ρ, T) -experimental data for [bmim][BF₄] and [bmim][PF₆] provide the structural estimates of hard-core volume, number of lattice sites in a cluster, and energy of near-neighbor pair interactions which are surprisingly close to ones independently predicted by the FT-model of a continuum substance.

Taking into account the compatibility of above results it is important to consider the presumable similarity between the square-well fluid (which may be thought of as a continuum analogue of the lattice-gas (LG) or lattice-fluid (LF) systems) on the one hand and the LJ-fluid of finite-range interactions (RPP) on the other. This conceptual analogy has been pointed out long ago for the critical region by Widom [21] who suggested that it is the propagation of attractive correlations in the LG which determines the peculiarities of criticality. However, such unphysical LG-predictions at low temperatures of the (ρ, T) -plane as the nonexistence of a (l, s) -transition suggest that repulsive forces are not being treated properly by this RPP-model. In contrast with the discrete LG-model, it seems that both attractive and repulsive forces are being dealt with properly in the square-well continuum fluid because it exhibits both (v, l) - and (l, s) -transitions. The serious restriction of latter is however evident since any singularities of RPP imply an artificial jump of pair-distribution isotropic function $g(r)$ at the point of cutoff radius r_c for attractive interactions.

In this context only the shifted and smoothed at r_c -point LJ-potential [5, 6] seems to be appropriate as RPP for a continuum system. Of course, the algebraic form of the respective reference EOS is essential too. In accordance with the statistical-mechanical arguments presented by Widom [21] there are the set of alternative forms including the original vdW-EOS and the LG-EOS in the well-known Bragg-Williams approximation which share the common restrictive feature. One may suppose that the probability of finding some prescribed value of the potential energy $U(\vec{r})$ at an arbitrary point in the fluid is independent of T at fixed ρ : $U(\vec{r}; \rho)$. Another simplifying assumption is that such EOS supposes only two types of fluid structure, one of the excluded (or hard-core) volume Nv_0 where the singular hard-sphere branch of potential is infinite and one of free volume $(V - Nv_0)$ where the potential is uniform, weak, and unrestricted (an infinite-range rectilinear well). It should be directly proportional to density $e = U/N = -a\rho$ where U is the total configurational energy and a is the constant vdW-coefficient. These historical notes are important to explain how one can go beyond the above restriction of T -independency by adoption of linear ρ -dependence for a generalized specific or molar energy (see also (8) below). Consider

$$a(T) = - \left(\frac{\partial e}{\partial \rho} \right)_T. \quad (5)$$

Another aim of the developed FT-EOS follows from the possibility [7] to estimate the effective LJ-parameters without any fit. Indeed, their general T -dependent values,

$$\sigma(T) = \left[\frac{3b(T)}{(2\pi N_A)} \right]^{1/3}; \quad (6a)$$

$$\frac{\varepsilon(T)}{k} = T(1 - Z_l), \quad (6b)$$

are determined simply in the low-temperature range of all ILs where b_0 is constant in ((1)–(4)) while the compressibility factor of saturated liquid $Z_l = P_\sigma/(\rho_l RT)$ becomes negligible as well as the vapor pressure $P_\sigma(T)$ trends to zero. Taking into account this asymptotic behavior it is especially important to study the possible correlations of these parameters in the RPP-model of an effective LJ-potential for ILs as the functions of total molecular weight M . This concept is unusual for the conventional consideration of a separate influence of the anion's M_a and cation's M_c components. It may provide, in principle, the useful insight the nature of (v, l) -transition in ILs by effective capturing underlying pair interactions.

The distinction of both FT-EOS and LF-EOS [14] from the conventional hard-sphere reference EOS is crucial to provide the quantitative description of one-phase liquid. The formers include the quadratic in density contribution, which is dominating at high pressures along the isotherms. The latter considers this term as a small vdW-perturbation for the hard-sphere EOS. Such perturbation approach is not directly applicable to associating fluids such as water and alcohols for which presence of hydrogen bonding, anisotropic dipolar $1/r^3$, or coulombic $1/r$ interactions in addition to isotropic dispersive $1/r^6$ attractions is inconsistent with the main assumption of the perturbation methodology that the structure of a liquid is dominated by repulsive forces [15].

The FT-model promotes the more flexible approach in which the above factors of attraction and clustering can be effectively accounted by the $a(T)$ -dependence. It was firstly confirmed by Longuet-Higgins and Widom and, then, by many authors that a combination of Carnahan-Starling EOS, for example, with the vdW-perturbation $a\rho^2$ is a reasonable approximation for the l - and s -phases but not the v -phase. Guggenheim [20] has concluded its applicability only to a liquid when large clusters are more important than small clusters (i.e., at low temperatures $T_m < T < T_b$). In contrast with this observation, the general FT-EOS provides the adequate representation of entire subcritical range $T_m < T < T_c$ including the critical region and (v, l) -phase transition [9–12]. It will be shown below by FT-model without undue complexity of calculations.

2. Universal FT-EOS for Any Low-Temperature Fluids

2.1. General Form of FT-EOS for Subcritical Temperatures. It is often claimed that the original van der Waals (vdW)-EOS

with two constant coefficients a, b determined by the actual critical-point properties ρ_c, T_c is only an approximation at best and cannot provide more than qualitative agreement with experiment even for spherical molecules. However, it was proved recently [9–12] that the general FT-EOS with three T -dependent coefficients,

$$P = \frac{\rho RT [1 - c(T)]}{1 - b(T)\rho} - a(T)\rho^2, \quad (7)$$

is applicable to any types of fluids including ILs. The measurable volumetric data of coexistence curve (CXC) have been used for evaluation of T -dependences without any fit. Consider

$$a(T) = \frac{P_\sigma(A_\sigma - 1)}{\rho_l \rho_g} = - \frac{(e_l - e_g)}{(\rho_l - \rho_g)}, \quad (8)$$

$$b(T) = \frac{A_\sigma - 2}{(\rho_l + \rho_g)(A_\sigma - 1)}, \quad (9)$$

$$1 - c(T) = Z_l \left[1 + \frac{\rho_l(A_\sigma - 1)}{\rho_g} \right] (1 - b\rho_l), \quad (10)$$

where the reduced slope $A_\sigma(T)$ of $P_\sigma(T)$ -function is defined by the thermodynamic Clapeyron's equation:

$$A_\sigma(T) = \frac{T}{P_\sigma} \frac{dP_\sigma}{dT} = \frac{T(s_g - s_l)\rho_l \rho_g}{P_\sigma(\rho_l - \rho_g)}. \quad (11)$$

This fundamental ratio of the (v, l) -latent heat to the thermodynamic work of (v, l) -expansion is the main parameter of FT-coefficients determined by ((8)–(9)). *It should be calculated separately in each of high-temperature ($T_b \leq T \leq T_c$) [9–12] v - and l -phases to obtain the reasonable quantitative prediction of one-phase thermophysical properties.* The general FT-EOS is applicable to the entire subcritical range ($T_t \leq T \leq T_c$) but it can be essentially simplified to the form of (1) if ($T_t \leq T \leq T_b$).

2.2. Particular Form of FT-EOS for Low Temperatures. An absence of input CXC-data $P_\sigma(T), \rho_g(T), \rho_l(T)$ for ILs is the serious reason to develop the alternative method for the evaluation of T -dependent FT-coefficients. The thermodynamically-consistent approach has been proposed in [7, 8] for the particular form of FT-EOS (1) applicable in the low-temperature range from the triple T_t (or melting T_m) point up to the T_b -point. Former one is usually known for ILs while the latter one is, as a rule, more than temperature of thermal decomposition $T_b > T_d \sim 650$ K. The methodology was tested on two low-molecular-weight substances (C_2H_4, H_2O) and two imidazolium-based ILs ([bmim][PF₆], [pmmim][Tf₂N]) with the promising accuracy of predictions even for the isothermal compressibility β_T up to the pressure $P = 200$ MPa.

To illuminate the distinction between the particular (reference) and general form of FT-EOS let us discuss in brief the main steps of the proposed procedure. Its detailed analysis can be found elsewhere [7, 8]. The algorithm is as follows.

Step 1. At the chosen free parameter T_b one determines the orthobaric molar densities $\rho_l(T_b) = \rho(T_b, P_0)$; $\rho_g(T_b) = P_0/RT_b$ to solve the transcendent equation:

$$\frac{\rho_g}{\rho_l} = \frac{1 + y(x) e^{-x}}{1 + y(x) e^x}, \quad (12)$$

for the reduced entropy (disorder) parameter $x(T_b)$ and the respective molar heat $r_\sigma(T_b)$ of vaporization. Consider

$$x = \frac{(s_g - s_l)}{2R}, \quad (13a)$$

$$r_\sigma = h_g - h_l = 2RT_b x(T_b). \quad (13b)$$

Step 2. The universal CXC-function $y(x)$ in (12) is determined by equalities

$$y(x) = \frac{\text{sh } x \text{ ch } x - x}{x \text{ ch } x - \text{sh } x}, \quad (14)$$

$$\text{sh } x = \frac{e^x - e^{-x}}{2}, \quad \text{ch } x = \frac{e^x + e^{-x}}{2},$$

and it provides the possibility to estimate a preliminary value of b_0 ,

$$b_0 = \frac{[x(T_b) - 1]}{\rho_l(T_b) [x(T_b) - 1/2]}, \quad (15)$$

as well as to evaluate the orthobaric densities at any T if the function $x(T)$ is known. Consider

$$\rho_g = \{b_0 [1 + y(x)e^x]\}^{-1}, \quad (16a)$$

$$\rho_l = \{b_0 [1 + y(x)e^{-x}]\}^{-1}. \quad (16b)$$

Step 3 (A-variant of $x(T)$ -prediction [7, 8]). To calculate its values one must obtain two densities $\rho^\pm$ (at the assumption $P_\sigma \approx 0$) from equation

$$\rho^\pm = \frac{1}{2b_0} \left[1 \pm \sqrt{1 - \frac{4b_0\rho(1-b_0\rho)}{1-Z_0(1-b_0\rho)}} \right], \quad (17)$$

where $\rho = \rho(T, P_0)$, $Z_0 = P_0/\rho RT$ and the $\rho^\pm(T)$ -function provides the preliminary estimate of $x(T)$ for the low-temperature range (at the consistent assumption: $\rho^+ \gg \rho_g \approx 0$). Consider

$$x(T) = \frac{1 - b_0\rho^+/2}{1 - b_0\rho^+}. \quad (18)$$

Step 4. One substitutes $x(T)$ from (18) in ((13a), (13b), (16a), (16b)) to calculate $r_\sigma(T)$, $\rho_g(T)$, $\rho_l(T)$, respectively.

Step 5. A preliminary value of $a_0(T)$ may be estimated then by the more restrictive assumption $P_0 \approx 0$ (used also in the famous Flory-Orwoll-Vrij EOS developed for heavy n -alkanes). Consider

$$a_0(T) = \frac{RT}{\rho_l(1 - b_0\rho_l)}. \quad (19)$$

TABLE 1: Coefficients of FT-EOS (1) for neutral (C_2H_4) and polar (H_2O) substances.

b_0 [dm ³ /mol], a [J·dm ³ /mol ²], T [K]			
C_2H_4 $b_0 = 0,04181$		H_2O $b_0 = 0,01658$	
T	a	T	a
103,99	1557,12	273,16	517,162
105	1459,76	278,15	527,171
110	1127,30	283,15	534,941
115	935,490	288,15	540,955
120	812,151	293,15	545,767
125	725,634	298,15	548,270
130	661,817	303,15	549,648
135	613,602	308,15	549,424
140	575,528	313,15	548,755
145	545,191	318,15	547,172
150	520,785	323,15	544,760
155	500,788	328,15	541,609
160	484,652	333,15	537,810
165	471,466	338,15	533,455
169,35	462,006	343,15	529,044
		348,15	524,605
		353,15	519,789
		358,15	514,676
		363,15	509,674
		368,15	504,480
		373,15	499,159

Step 6 (B-variant of $x(T)$ -prediction). To control the consistency of methodology one may use instead of Step 3 (A-variant) the same equation (17) with the approximate equality $\rho_l(T) \approx \rho^+(T)$ to solve (16b) at the a priori chosen b_0 -value for determination of alternative $x(T)$, and so forth, (Steps 4 and 5). *Just this approach (B-variant) has been used below in the low-temperature range of [bmim][BF₄].*

Step 7. The self-consistent prediction of a hypothetical (v, l)-diagram requires the equilibration of CXC-pressures $P_\sigma(T, \rho_g) = P_\sigma(T, \rho_l)$ by FT-EOS (1) with the necessary final change in $a_0(T)$ -value from (19) to satisfy the equality

$$a(T) = a_0(T) - \frac{P_\sigma(T, \rho_g)}{\rho_l^2}. \quad (20)$$

Only in the low-temperature range $T \leq T_b$ the distinction between the preliminary definition (18) and its final form (19) for $a(T)$ -values is not essential at the prediction of vapor pressure $P_\sigma(T, \rho_g)$.

3. Reference Equation of State, Effective Pair Potential, and Hypothetical Phase Diagram

To demonstrate universality of approach and for convenience of reader we have collected the coefficients of FT-EOS (1) for neutral (C_2H_4) and polar (H_2O) fluids [7, 8] in Table 1 and

TABLE 2: Coefficients of FT-EOS (1) for ILs: [bmim][PF₆], [pmmim][Tf₂N], and [bmim][BF₄].

b_0 [dm ³ /mol], a [J·dm ³ /mol ²], T [K]					
[bmim][PF ₆] $b_0 = 0,1953$		[pmmim][Tf ₂ N] $b_0 = 0,2711$		[bmim][BF ₄] $b_0 = 0,178$	
T	a	T	a	T	a
285	8433,52	288,15	11724,8	290	9470,0
290	8214,24	295,15	12224,5	300	8900,9
295	8015,04	304,25	12279,0	310	8435,0
300	7833,44	313,65	11728,9	320	8047,5
305	7667,34	324,35	11308,4	330	7720,8
310	7514,97	335,15	10672,3	340	7442,2
315	7374,83	344,65	10051,1	350	7202,6
320	7245,64	350,15	9709,50		
325	7126,31				
330	7015,89				
335	6913,55				
340	6818,59				
345	6730,37				
350	6648,36				

added in Table 2 to other ILs ([bmim][PF₆], [pmmim][Tf₂N] [7, 8]) the data for [bmim][BF₄] obtained in this work (Table 3). When temperature is low $T_m < T < T_b$ FT-model follows a two-parameter ($\varepsilon(T), \sigma_0$) correlation of principle of corresponding states (PCS) on molecular level as well as a two-parameter ($a(T), b_0$) correlation of PCS on macroscopic level.

One the most impressed results of FT-methodology is shown in Figure 1 where the comparison between such different high- and low-molecular substances as ILs and C₂H₄, H₂O is represented. The results based on the coefficients of Tables 1 and 2 demonstrate that the proposed low-temperature model provides the symmetric two-value representation of vapor pressure $\pm P_s(T)$ similar to that observed for the ferromagnetic transition in weak external fields.

To estimate the appropriate excluded molar volume b_0 ($M = 225,82$ g/mol) of FT-model we consider that it belongs to the range [$v_0 = M/\rho_0 \approx 162$, $v_l = M/\rho_l \approx 187$ cm³/mol]. The extrapolated to zero temperature $T = 0$ K “cold” volume $v_0 = 162$ cm³/mol follows from (27). The fixed value: $b_0 = 178$ cm³/mol ($b_0 \approx 1,1v_0$) has been used in this work to demonstrate the main results of the proposed methodology. Such choice for [bmim][BF₄] on the ad hoc basis is in a good correspondence with the respective values: $b_0 = 195,3$ cm³/mol for [bmim][PF₆] and $b_0 = 271,1$ cm³/mol for [pmmim][Tf₂N] where the empirical relationship $b_0 \approx 1,1v_0$ was also observed [7, 8]. Our estimates of the effective LJ-diameters by (6a) for ILs: $\sigma([bmim][BF_4]) = 5,208$ Å, $\sigma([bmim][PF_6]) = 5,371$ Å, and $\sigma([pmmim][Tf_2N]) = 5,992$ Å can be tested by comparison with the independently determined values [13] for anions $\sigma_a([BF_4]) = 4,51$ Å; $\sigma_a([PF_6]) = 5,06$ Å. We have verified Berthelot’s combining rule for spherical molecular ions (21a) and van der Waals’ combining

(a)

(b)

FIGURE 1: (a) Comparison of the predicted two-value vapor pressures $\pm P_s^g$ ($-P_s^g \approx P_l^-$) with the tabular $P_s(T)$ -data for ethylene [23] and water [24]; (b) predicted two-value vapor pressures $\pm P_s^g$ ($-P_s^g \approx P_l^-$) for [bmim][PF₆] and [pmmim][Tf₂N].

rule for chain molecules (21b) usually considered by van der Waals’-type of EOS for mixtures [22]. Consider

$$\sigma = \frac{\sigma_c + \sigma_a}{2}, \quad (21a)$$

$$b_0 = \frac{b_c + b_a}{2}. \quad (21b)$$

The predicted by former rule of LJ-diameter for the same [bmim]-cation were close but still different, 5,906 Å and 5,682 Å. For the latter rule their values and distinction become even smaller, 5,757 Å and 5,651 Å. As a result, the chain rule (21b) seems preferable for ILs and its average value for $\sigma_c[\text{bmim}] = 5,704$ Å can be used to estimate the LJ-diameter of [Tf₂N]-anion: $\sigma_a[\text{Tf}_2\text{N}] = 6,254$ Å taking into account the equality: $M_c[\text{bmim}] = M_c[\text{pmmim}] = 139$ g/mol.

TABLE 3: Predicted hypothetical (v, l)-transition in the low-temperature range for FT-model of [bmim][BF₄] based on the experimental data [1, 2] treated by FT-EOS (B -variant of $x(T)$ -prediction).

T (K)	ρ_l (mol/dm ³)	ρ_g (mol/dm ³)	P_σ (kPa)	r_σ (J/mol)	a (J·dm ³ /mol ²)	ε/k (K)
290	5,350646	3,09E – 08	7,45E – 05	53082	9470,0	290
300	5,322170	2,1E – 07	5,24E – 04	49866	8900,9	300
310	5,293693	1,01E – 06	0,002	47230	8435,0	309,99
320	5,265215	3,74E – 06	0,009	45032	8047,5	319,99
330	5,236735	1,13E – 05	0,031	43175	7720,8	329,99
340	5,208254	2,92E – 05	0,082	41587	7442,2	339,99
350	5,179771	6,61E – 05	0,192	40216	7202,6	349,99
360	5,151287	0,000135	0,404	39022	6994,6	359,99
370	5,122802	0,000253	0,778	37974	6813,0	369,98
380	5,094315	0,000441	1,393	37048	6653,5	379,96
390	5,065828	0,000725	2,347	36225	6512,7	389,94
400	5,037338	0,001131	3,754	35488	6387,8	399,91
410	5,008848	0,001689	5,740	34826	6276,6	409,86
420	4,980355	0,002428	8,446	34228	6177,4	419,79
430	4,951862	0,003379	12,017	33684	6088,7	429,70
440	4,923367	0,004569	16,604	33188	6009,1	439,59
450	4,894871	0,006027	22,359	32733	5937,6	449,45
460	4,866373	0,007778	29,432	32314	5873,2	459,27
470	4,837873	0,009843	37,968	31926	5815,4	469,05
480	4,809372	0,012244	48,105	31566	5763,2	478,79
490	4,780869	0,014997	59,977	31230	5716,3	488,49
500	4,752365	0,018119	73,704	30914	5674,1	498,13
510	4,723859	0,021622	89,400	30618	5636,1	507,72
511	4,721008	0,021993	91,082	30589	5632,5	508,67
512	4,718157	0,022369	92,785	30561	5629,0	509,63
513	4,715307	0,022748	94,509	30532	5625,4	510,58
514	4,712456	0,023132	96,254	30504	5622,0	511,54
515	4,709605	0,023519	98,020	30476	5618,6	512,49
516	4,706754	0,023910	99,806	30448	5615,2	513,44
517	4,703903	0,024306	101,615	30420	5611,8	514,40

TABLE 4: Effective LJ-diameters of FT-model for ILs determined by (6a), (6b), and (21b) on the base of estimates [7, 13] and the choice $b_0 = 178$ cm³/mol for [bmim][BF₄] in this work.

IL	M (g/mol)	σ (Å)	M_c/M_a	σ_c/σ_a
[bmim][BF ₄]	225,82	5,208	139/86,82	5,757/4,51 [13]
[bmim][PF ₆]	284	5,371 [7]	139/145	5,651/5,06 [13]
[pmmim][Tf ₂ N]	419,1	5,992 [7]	139/280,1	5,704/6,254

The collected in Table 4 effective LJ-diameters are linear functions of M_a in the set of ILs with different anions and cations if the molecular weight of latters M_c is the same one.

Since the low-temperature compressibility factor $Z_l(T)$ is very small for all discussed liquids their dispersive energies $\varepsilon(T)$ (molecular attraction's parameters) are comparable in accordance with (6b). However, the differences in cohesive energies $a(T)$ (collective attraction's parameters) between the low-molecular substances (C₂H₄, H₂O) and ILs are striking as it follows from Tables 1 and 2. The physical nature of such

distinction can be, at the first glance, attributed to omitted in the reference LJ-potential influence of intramolecular force-field parameters and anisotropic (dipole-dipole and coulombic) interactions. At the same time, one must account the collective macroscopic nature of $a(T)$ -parameter. It corresponds to the scales which are compatible or larger than the thermodynamic correlation length $\xi(\rho, T)$. FT-model [9–12] provides an elegant and simple estimation of this effective parameter based on the concept of comparability between energetic and geometric characteristic of force field determined by the given RPP. Consider

$$\xi^3 = \frac{a(T)}{k_B T} - \frac{\varepsilon(T)}{\rho k_B T} = \frac{b_0}{1 - b_0 \rho}. \quad (22)$$

Taking into account the above results and the coefficients from Tables 1–3 we have used (22) at $T = 300$ K ($T^* = k_B T/\varepsilon \approx 1$) to compare the thermodynamic correlation length predicted for [bmim][BF₄] ($a = 8900,9$ J·dm³/mol²; $b_0 = 178$ cm³/mol; $\rho = 5,322294$ mol/dm³) and at $T = 298,15$ K for water ($a = 548,27$ J·dm³/mol²; $b_0 = 16,58$ cm³/mol;

FIGURE 2: Comparison of the GEMC-simulated (black triangles) (v, l)-diagram [6] for [bmim][BF₄] with the HPD-predicted coexistence of orthobaric densities (lines with black squares); the characteristic (T_c, T_b) points are emphasized as well as the distinction of respective rectilinear [6] and strongly-curved (HPD) diameters. The input low-temperature experimental $\rho_l(P_o, T)$ -data [1, 2] are represented by white diamonds. Location of classical spinodal and its critical point ($\square$) predicted by LF-EOS [14] is shown by dashed line.

FIGURE 3: Enthalpy of vaporization for [bmim][BF₄] calculated by different methodologies (GEMC-simulated [6] ($\blacktriangle, \blacktriangle$); FT-EOS-predicted at $T \leq T_b$ ($\blacksquare, \blacksquare$); HPD-predicted ($\blacksquare, \blacksquare$); tabular data for water [24] ($\blacklozenge, \blacklozenge$)).

$\rho = 55,444 \text{ mol/dm}^3$ [24]. The dimensional and reduced ($\xi^* = \xi/\sigma$) values for former are, respectively, $\xi = 177,7 \text{ \AA}$, $\xi^* = 34,12$ while for latter $\xi = 69,86 \text{ \AA}$, $\xi^* = 29,45$. *No more need be said to confirm the universality of FT-model.*

One may note that our estimates of correlation length are significantly larger than those usually adopted for the dimensional or reduced cutoff radius (r_c or $r_c^* = r_c/\sigma$) of direct interactions at computer simulations. As a result, the standard assumption $\xi_c^* \approx r_c^*$ may become questionable in the comparatively small (mesoscopic) volumes of simulation $L^3 < \xi(\rho, T)^3$. At this condition the simulated properties are mesoscopic although their lifetime may be essentially larger than its simulated counterpart. The key point here is the same as one near a critical point where the problem of

FIGURE 4: Comparison of the GEMC-simulated [6] pressures of condensation ($\blacktriangle, \blacktriangle$) with the HPD-predicted pressures of boiling ($\blacksquare, \blacksquare$) for [bmim][BF₄]. The characteristic (T_c, T_b) points are emphasized; tabular data for water [24] ($\blacklozenge, \blacklozenge$). The location of spinodal predicted by LF-EOS [14] is shown by dashed line.

consistency between the correlation length for statics and the correlation time for dynamics becomes crucial. In any case, the computer study of possible nongaussian nature of local fluctuations within the thermodynamic correlation volume ξ^3 may be quite useful. The relevant inhomogeneities in the steady spacial distributions of density and enthalpy can affect, first of all, the simulated values of volumetric (α_p, β_T) and caloric (C_p, C_v) derived quantities. Simultaneously, an account of internal degrees of freedom and anisotropy by the perturbed RPP may change the correlation length itself.

The above described by ((12)–(20)) FT-methodology has been used to reconstruct the hypothetical phase diagram (HPD) for [bmim][BF₄] shown in Figures 2, 3, and 4 and represented in Table 3. Both (T, ρ) (Figure 2) and (P, T) (Figure 4) projections contain also the branches of classical spinodal calculated by the LF (Sanchez-Lacombe)-EOS obtained in [14]. Its top is the location of a respective critical point. It seems that the relatively close (P_c, T_c)-parameters predicted independently by FT-EOS and by LF-EOS (see Section 1) are reasonable.

The FT-model provides a possibility to estimate, separately, the coordination numbers of LJ-particles in the orthobaric liquid $\rho_l(T)$ - and vapor $\rho_g(T)$ -phases. An ability to form the respective “friable” ($N_{l,g} + 1$)-clusters is defined by the ratio of effective cohesive and dispersive molar energies at any subcritical temperature. Consider

$$N_{l,g} = \frac{a_{l,g}(T) \rho_{l,g}}{RT(1 - Z_l)}. \quad (23)$$

The term “friable” is used here to distinguish the clusters formed by the unbounded LJ-particles at the characteristic distance $l^* = l/\sigma \approx \sqrt[3]{2} > 1$ from the conventional “compact” ones with the bonding distance $l^* < 1$ studied, in particular, by the GEMC-methodology [25] to model of molecular association. It is straightforwardly to obtain the low-temperature estimates based on the assumptions.

FIGURE 5: Comparison of two coordination numbers N_l predicted by FT-EOS to characterize the clustering in an orthobaric liquid of [bmim][BF₄] at $T \leq T_b$ (■) and in the entire (v,l) -range of HPD (◆); FT-EOS predictions for water are shown as —◆ at $T \leq 373$ K.

$$Z_l \ll Z_g \approx 1,$$

$$N_l \approx \frac{1}{1 - b_0 \rho_l}, \quad (24a)$$

$$N_g \approx \frac{b_0 \rho_g}{1 - b_0 \rho_g}, \quad (24b)$$

and to find the critical asymptotics based on the difference of classical (a^0, b^0, c^0) and nonclassical (a, b, c) T -dependent FT-EOS' coefficients [9–12]. Consider

$$N_l^c = \frac{3Z_c}{1 - Z_c}, \quad (25a)$$

$$N_g^c = \frac{Z_c}{1 - Z_c} \left[\frac{A_c (1 - b_c^0 \rho_c)}{1 - b_c \rho_c} - 1 \right]. \quad (25b)$$

The crucial influence of excluded-volume in (24a) and its relative irrelevance in (24b) for $N_{l,g}$ -predictions are illustrated by Figure 5 where $N_l(T)$ function is shown also for the entire l -branch based on the evaluated in the present work HPD. For comparison, the low-temperature ability to form the $(N_l + 1)$ -clusters in liquid water [7, 24] is represented in Figure 5 too.

In according with ((25a), (25b)) the “friable” clusters can exist only as dimers in the *classical critical liquid phase* ($N_l^c \approx 1$). It is not universal property in the meaning of scaling theory but it corresponds to the PCS-concept of similarity between two substances (H₂O and [C₄mim][BF₄], e.g.) if their Z_c -values are close. On the other side, the scaling hypothesis of universality is confirmed by the FT-EOS' estimates in the *nonclassical critical vapor phase*. For the set of low-molecular-weight substances studied in [9] (Ar, C₂H₄, CO₂, H₂O); for example, one obtains by (25b) the common estimate ($N_g^c \approx 2.5$) which shows a significant associative near-mean-field behavior.

It is worthwhile to note here the correspondence of some FT-EOS'-estimates with the set of GEMC-simulated

results. One may use the approximate estimate of critical slope $A_c \approx 7.86$ [9] for [bmim][BF₄] based on the similarity of its Z_c -value with that for H₂O [24]. In such case, the respective critical excluded volume $b_c \approx 220$ cm³/mol becomes much more than vdW-value $1/3\rho_c = b_c^0 \approx b_0 \approx 178$ cm³/mol. Another observation seems also interesting. Authors [25] have calculated (see Figure 3 in [25]) for the “compact” clusters at $l^* = 0.7, 0.5, 0.45$; the (T^*, ρ^*) -diagram of simple fluids. One may note that only the value $l^* = 0.7$ corresponds to the shape of strongly-curved diameter shown in Figure 2 for the HPD while the smaller values: $l^* = 0.5, 0.45$ give the shape of HPD and the nearly rectilinear diameter strongly resembling those obtained by the GEMC-simulations [6] for the complex ILs force-field. If this correspondence between the “friable” and “compact” clustering is not accidental one obtains the unique possibility to connect the measurable thermophysical properties with the both characteristics of molecular structure in the framework of FT-EOS.

4. Comparison with the Empirical Tait EOS and Semiempirical Sanchez-Lacombe EOS

The empirical Tait EOS is based on the observation that the reciprocal of isothermal compressibility β_T^{-1} for many liquids is nearly linear in pressure at very high pressures. Consider

$$1 - \frac{\rho(P_0, T)}{\rho(P, T)} = C(T) \ln \left[\frac{B(T) + P}{B(T) + P_0} \right], \quad (26)$$

where some authors [14, 19] omit the T -dependence in coefficient C and ignore the value $P_0 \approx 0$ [14]. Such restrictions transform the Tait EOS into the empirical form of two-parameter $(B(T), C)$ PCS because the sets of C -values for different ILs become close one to another. For example, Machida et al. [14] have found the sets $C = 0.09710$ for [bmim][PF₆], $C = 0.09358$ for [bmim][BF₄], and $C = 0.08961$ for [bmim][OCSO₄] which is rather close to the set obtained by Matkowska and Hofman [19] $C = 0.088136$ for [bmim][BF₄] and $C = 0.0841547$ for [bmim][MeSO₄]. At the same time, Gu and Brennecke [3] have reported the much larger T -dependent values $C(298, 2 \text{ K}) = 0.1829$ and $C(323, 2 \text{ K}) = 0.1630$ for the same [bmim][PF₆].

Two other reasons of discrepancies in the Tait methodology is the different approximations chosen by authors for the reference input data $\rho(P_0, T)$ and for the compound-dependent function $B(T)$. Some authors [4, 14, 18] prefer to fit the atmospheric isobars $\rho(P_0, T)$ and $C_p(P_0, T)$ with a second-order or even third-order polynomial equation while the others [1, 2, 16, 19] use a linear function for this aim.. As a result, the extrapolation ability to lower and higher temperatures of different approximations becomes restricted.

In this work we have used for [bmim][BF₄] the simplest linear approximation of both density and heat capacity,

$$\begin{aligned}\rho(P_0, T) &= \rho_0 \left(1 - \frac{T}{T_0}\right) \\ &= 1394,65 \left(1 - \frac{T}{2170,44}\right) \text{ kg}\cdot\text{m}^{-3},\end{aligned}\quad (27)$$

$$\begin{aligned}C_p(P_0, T) &= C_p^0 \left(1 + \frac{T}{T_0}\right) \\ &= 273,65 \left(1 + 9,537 \cdot 10^{-4} T\right) \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1},\end{aligned}\quad (28)$$

taken from [1]. The extrapolated to zero of temperature value $\rho_0(0 \text{ K}) = 1394,65 \text{ kg}\cdot\text{m}^{-3}$ [1] is in a good correspondence with that from [14] $\rho_0(0 \text{ K}) = 1393,92 \text{ kg}\cdot\text{m}^{-3}$, in reasonable correspondence with that from [19] $\rho_0(0 \text{ K}) = 1416,03 \text{ kg}\cdot\text{m}^{-3}$ and that from [16] $\rho_0(0 \text{ K}) = 1429 \text{ kg}\cdot\text{m}^{-3}$ but its distinction from value $\rho_0(0 \text{ K}) = 1476,277 \text{ kg}\cdot\text{m}^{-3}$ reported by authors [18] is rather large. The similar large discrepancy is observable between $C_p^0(0 \text{ K}) = 273,65 \text{ J/mol}\cdot\text{K}$ from [1] and $C_p^0(0 \text{ K}) = 464,466 \text{ J/mol}\cdot\text{K}$ from [18].

The different choices of an approximation function for $B(T)$ (so authors [14] have used the exponential form while authors [19] have preferred the linear form) may distort the derivatives β_T and α_P calculated by the Tait EOS (26). The problem of their uncertainties becomes even more complex if one takes into account the often existence of systematic distinctions of as much as 0,5% between the densities measured by different investigators even for the simplest argon [23]. Machida et al. [14], for example, pointed out the systematic deviations measured densities from those reported by the de Azevedo et al. [18] and Fredlake et al. [1] for both [bmim][BF₄] and [bmim][PF₆]. Matkowska and Hofman [19] concluded that the discrepancies between the different sets of calculated β_T - and α_P -derivatives increase with increasing of T and decreasing of P due not only to experimental differences in density values but also result from the fitting equation used. The resultant situation is that the expansivity α_P of ILs reported in literature was either nearly independent of T [18] or noticeably dependent of T [3, 19].

We can add to these observations that the linear in molar (or specific) volume Tait Eos (26) is inadequate in representing the curvature of the isotherm $P(\rho)$ at low pressures. It fails completely in description of (v, l) -transition where the more flexible function of volume is desirable. However, this has been clearly stated and explained by Streett for liquid argon [23] that the adjustable T -dependence of empirical EOS becomes the crucial factor in representing the expansivity α_P and, especially, heat capacities C_p , C_v at high pressures even if the reliable input data of sound velocity $W(P, T)$ were used.

From such a viewpoint, one may suppose that the linear in temperature LF-EOS proposed by Sanchez and Lacombe,

$$\bar{P} = -\bar{\rho}^2 - \bar{T} \left[\ln(1 - \bar{\rho}) + \left(1 - \frac{1}{N_l}\right) \bar{\rho} \right], \quad (29)$$

is restricted to achieve the above goal but can be used as any unified classical EOS common for both phases to predict the region of their coexistence. Such conjecture is confirmed by the comparison of FT-EOS with LF-EOS presented in Figures 2 and 4 and discussed below. The obvious advantage of former is the more flexible T -dependence expressed via the cohesive-energy coefficient $a(T)$. On the other hand, the LF-EOS is typical form of EOS (see Section 1) in which the constraint of T -independent potential energy $U(\vec{r}; \rho)$ is inherent [21].

One may consider it as the generalized variant of the well-known Bragg-Williams approximation for the ordinary LG presented here in the dimensional form

$$P = -a\rho^2 - \frac{k_B T}{v_0} \ln(1 - \rho v_0). \quad (30)$$

Such generalization provides the accurate map of phenomenological characteristic parameters T^* , P^* , ρ^* which determine the constant effective number of lattice sites N_l occupied by a complex molecule,

$$N_l = \frac{P^* M}{\rho^* R T^*} = \frac{M}{v^* \rho^*} = \frac{M P^*}{\varepsilon^* \rho^*}, \quad (31)$$

into the following set of molecular characteristic parameters for a simple molecule ($N_l = 1$):

$$\rho^* = \frac{1}{v_0}, \quad P^* = \frac{z\varepsilon}{2v_0}, \quad T^* = \frac{z\varepsilon}{2k_B}, \quad (32)$$

where v_0 is the volume of cell and z is the coordination number of lattice in which the negative ε is the energy of attraction for a near-neighbor pair of sites. In the polymer terminology ε^* from (31) is the segment interaction energy and v^* is the segment volume which determines the characteristic hard core per mole M/ρ^* (excluded volume b in the vdW-terminology).

Another variant of described approach is the known perturbed hard-sphere-chain (PHSC) EOS proposed by Song et al. [15] for normal fluids and polymers

$$\frac{P}{\rho k_B T} = 1 + g(d) b N_l^2 \rho - [g(d) - 1] (N_l - 1) - \frac{a N_l^2 \rho}{k_B T}, \quad (33)$$

where $g(d) = (1 - \eta/2)/(1 - \eta)^3$ is the pair radial distribution function of nonbonded hard spheres at contact and the term with $(N_l - 1)$ reflects chain connectivity while the last term is the small perturbation contribution. Though the PHSC-EOS has the same constraint of the potential energy field $U(\vec{r}; \rho)$ authors [15] have introduced two universal adjustable

$\Phi_a(T)$ - and $\Phi_b(T)$ -functions to improve the consistency with experiment. The vdW-type coefficients were rescaled as

$$a(T) = \left(\frac{2\pi}{3}\right) \sigma^3 \varepsilon \Phi_a\left(\frac{\bar{T}}{s}\right), \quad (34a)$$

$$b(T) = \left(\frac{2\pi}{3}\right) \sigma^3 \Phi_b\left(\frac{\bar{T}}{s}\right), \quad (34b)$$

where $s(N_l)$ is the additional scaling function for $T^* = \varepsilon/k_B$. It provides the interconnection of molecular LJ-type parameters (ε, σ) with the phenomenological vdW-ones (a, b). The resultant reduced form of PHSC is [15]

$$\begin{aligned} \bar{P} = -\bar{\rho}^2 \Phi_a\left(\frac{\bar{T}}{s}\right) \\ - \bar{T} \left[-\bar{\rho} - g(d) \Phi_b\left(\frac{\bar{T}}{s}\right) \bar{\rho}^2 + \left(1 - \frac{1}{N_l}\right) g(d) \bar{\rho} \right], \end{aligned} \quad (35)$$

where the following characteristic and reduced variables are used:

$$\begin{aligned} \bar{\rho} = \frac{2\pi\sigma^3}{3} N_l \rho = \frac{\rho}{\rho^*}, \quad \bar{T} = \frac{k_B T}{\varepsilon} = \frac{T}{T^*}, \\ \bar{P} = \frac{P}{k_B T^* \rho^* N_l} = \frac{P}{P^*}. \end{aligned} \quad (36)$$

It was compared with the simpler form of LF-EOS (29). Their predictions of the low-temperature density at saturation $\rho_l(T)$ are comparable but, unfortunately, inaccurate (overestimated) even for neutral low-molecular liquids. The respective predictions of the vapor pressure $P_\sigma(T)$ are reasonable [15] excepting the region of critical point for both EOSs. Our estimates based on the LF-EOS [14] shown in Figures 2 and 4 are consistent with these conclusions.

The comparison of volumetric measurements and derived properties [14, 18] with the purely predictive (by the FT-EOS) and empirical (by the Tait EOS and LF-EOS) methodologies used for [bmim][BF₄] is shown in Figures 6–9. Evidently, that former methodology is quite promising. Machida et al. [14] have reported two correlations of the same (P, ρ, T) -data measured for [bmim][BF₄] at temperatures from 313 to 473 and pressures up to 200 MPa. To examine the trends in properties of ILs with the common cation [bmim] the Tait empirical EOS was preliminarily fitted as the more appropriate model. The estimate of its extrapolation capabilities for (P, ρ, T) -surface in the working range ($290 < T/K < 350$) follows from the compatibility of experimental points (where those measured by de Azevedo et al. [18] in the range of temperature $298 < T/K < 333$ and pressure ($0,1 < P/\text{MPa} < 60$) were also included) with the thick curves in Figure 6. It is noticeable, for example, that the extrapolated Tait's isotherm $T = 290$ K coincides practically with isotherm $T = 298,34$ K from [18] because the measured densities of latter source are systematically higher than those from [14]. Density data of Fredlake et al. [1] for [bmim][BF₄] (not shown in Figure 6) are also systematically shifted from measurements [14].

FIGURE 6: Comparison of experimental densities for [bmim][BF₄] (○-298,34 [18]; □-313,01 [18]; △-322,85 [18]; ◇-332,73 [6]; ■-313,1 [14]; ◆-332,6 [14]; ▲-352,6 [14]) with those calculated: (a) by the Tait EOS [14] (in a working range $290 < T/K < 350$ via the interval 10 K thick continuous curves); (b) by the Sanchez-Lacombe EOS [14] (thick dashed curves); (c) by the FT-EOS (thin continuous curves).

FIGURE 7: Comparison of isobaric expansivities for [bmim][BF₄] calculated: (a) by the Tait EOS [14]; (b) by the Sanchez-Lacombe EOS [14]; (c) by the FT-EOS.

The consequence of such discrepancies is also typical for any simple liquids (Ar, Kr, Xe) [23] at moderate and high pressures. It is impossible to reveal an actual T -dependence of volumetric (mechanical) derived functions α_p, γ_p due to systematic deviations between the data of different investigators. In such situation an attempt “to take the bull by the horns” and to claim the preferable variant of EOS based exclusively on volumetric data may be erroneous. Indeed, since the Tait EOS is explicit in density while the LF-EOS—in temperature the direct calculation of α_p, β_T -derivatives for former and α_p, γ_p -derivatives for latter are motivated. To illustrate the results of these alternative calculations we have used in Figures 6–9 the coefficients of LF-EOS reported by Machida et al. [14] for the restricted range of moderate pressures $0,1 < P/\text{MPa} < 50$. The thick dashed curves represent

FIGURE 8: Comparison of isothermal compressibilities for [bmim][BF₄] calculated: (a) by the Tait EOS [14]; (b) by the Sanchez-Lacombe EOS [14]; (c) by the FT-EOS.

FIGURE 9: Comparison of thermal pressure coefficient for [bmim][BF₄] calculated: (a) by the Tait EOS [14]; (c) by the FT-EOS.

the boundaries of working range where the extrapolation to $T = 290$ K is again assumed. One may notice the qualitative similarity of FT-EOS (the thin curves) and LF-EOS which can be hypothesized as an existence of certain model substance at the extrapolation to higher pressures $P/\text{MPa} > 50$. It demonstrates the smaller compressibility β_T (Figure 8) and expansivity α_p (Figure 7) than those predicted by the Tait EOS while the value of thermal-pressure coefficient γ_p for FT-EOS (Figure 9) becomes larger. It determines the distinctions in the calculated internal pressure. The choice of the FT-model's substance as a reference system for the perturbation methodology provides the set of advantages in comparison with the LF-EOS.

It follows from Figure 6 that at moderate pressures $P/\text{MPa} < 50$ the predictive FT-EOS is more accurate than the fitted semiempirical LF-EOS [14] although the discrepancies of both with the empirical Tait EOS [14] become significant at the lowest (extrapolated) temperature $T = 290$ K.

FIGURE 10: Comparison of predicted by FT-EOS isochoric heat capacity for [bmim][BF₄] (lines) with that evaluated by de Azevedo et al. [18] (points) on the base of speed velocity and density input data.

The Tait's liquid has no trend to (v, l) -transition (as well as polymers) in opposite to the clear trends demonstrated by FT-EOS and LF-EOS. One may suppose [26] a competition between vaporization of IL (primarily driven by the isotropic dispersive attraction $1/r^6$ in RPP) and chain formation (driven mainly by the anisotropic dipolar interactions $1/r^3$) reflected by the Tait EOS fitted to the experimental data. Of course, such conjecture must be, at least, confirmed by the computer simulations and FT-model provides this possibility by the consistent estimate of RPP-parameters (ϵ, σ) at each temperature.

The differences of calculated expansivity α_p in Figure 7 are especially interesting. FT-EOS predicts even less variation of it with temperature than that for the Tait EOS. This result and crossing of $\alpha_p(P)$ -isotherms are qualitatively similar to those obtained by de Azevedo et al. [18] although the pressure dependence of all mechanical ($\alpha_p, \beta_T, \gamma_p$) and caloric (C_p, C_v) derivatives (see Figures 10, 11, and 12) is always more significant for the FT-EOS predictions. It seems that the curvature of the $\rho(T)$ -dependence following from the LF-EOS (29) is not sufficient to predict the $\alpha_p(P)$ behavior (Figure 7) correctly. The strong influence of the chosen input $\rho(P_0, T)$ -dependence is obvious from Figures 7–9.

The prediction of caloric derivatives ($C_p, C_v, C_p/C_v, Gr$) is the most stringent test for any thermal (P, ρ, T) EOS. It should be usually controlled [23] by the experimental (W, ρ, T)-surface to use the thermodynamical identities,

$$C_p = C_v + \frac{T\alpha_p\gamma_p}{\rho}, \quad (37)$$

$$W = \sqrt{\frac{C_p}{M(C_p\beta_T\rho - T\alpha_p^2)}}, \quad (38)$$

$$Gr = \frac{MW^2\alpha_p}{C_p} = \frac{1}{T\alpha_p} \left(\frac{C_p}{C_v} - 1 \right), \quad (39)$$

FIGURE 11: Comparison of predicted by FT-EOS isobaric heat capacity for [bmim][BF₄] (lines) with that evaluated by de Azevedo et al. [18] (points) on the base of speed velocity and density input data.

FIGURE 12: Comparison of predicted by FT-EOS ratio of heat capacities for [bmim][BF₄] (thin lines) with that evaluated by de Azevedo et al. [18] on the base of speed velocity and density input data (thick lines).

in addition to the chosen input $C_p(P_0, T)$ -dependence. de Azevedo et al. [18] applied this strategy to comprise the approximated by the Pade-technique measured speed of sound data for [bmim][PF₆] and [bmim][BF₄] (Figure 13) with the evaluated at high pressures heat capacities.

Our predictive strategy is based [17] on the differentiation of $a(T)$ -dependence to evaluate directly the most subtle (C_v, P, T) -surface in a low-temperature liquid

$$C_v(P, T) = C_v(P_0, T) - \frac{da}{dT} [\rho(P, T) - \rho(P_0, T)], \quad (40)$$

where the influence of the consistence for the chosen input $\rho(P_0, T)$ - and $C_p(P_0, T)$ -dependences (via (37) used for estimate of $C_v(P_0, T)$ at the atmospheric pressure P_0) becomes crucial. The use of first derivative da/dT (even by its rough approximation in terms of finite differences: $\Delta a/\Delta T$) to

FIGURE 13: Comparison of predicted by FT-EOS speed of sound for [bmim][BF₄] (thin lines) with that (points) used by de Azevedo et al. [18] as the input data (see also Figure 5 for density used by de Azevedo et al. [18] as the input data at evaluations).

calculate simultaneously by ((3), (4), (37), (40)) all volumetric and caloric derivatives is the important advantage over the standard integration of thermodynamic identities:

$$\left(\frac{\partial C_v}{\partial v}\right)_T = T \left(\frac{\partial^2 P}{\partial T^2}\right)_v, \quad (41a)$$

$$\left(\frac{\partial C_p}{\partial P}\right)_T = -T \left(\frac{\partial^2 v}{\partial T^2}\right)_P. \quad (41b)$$

To illustrate such statement it is worthwhile to remind the situation described by the Streett [23] for liquid argon. Since isotherms of $\alpha_p(P)$ cross over for many simple liquids (Ar, Kr, Xe), this author concludes that the sign of $(\partial^2 v/\partial T^2)_P$ changes also from positive to negative at the respective pressure. This conclusion is not valid because to change the sign of derivative $(\partial \alpha_p/\partial T)_P$ it is enough to account for the exact equality

$$\left(\frac{\partial \alpha_p}{\partial T}\right)_P = -\alpha_p^2 + \frac{1}{v} \left(\frac{\partial^2 v}{\partial T^2}\right)_P, \quad (42)$$

in which $(\partial^2 v/\partial T^2)_P$ can be always positive. In this case one would expect the monotonous decrease of C_p with increasing P in accordance to ((41a), (41b)) while the presence of extremum (minimum or maximum of $C_p(P)$ -dependence) seems to be artificial.

There is the variety of pressures reported by different investigators as a presumable cross-point for the same ILs. Machida et al. [14] have estimated it to be about 10 MPa on the base of Tait EOS for [bmim][PF₆] but have not found it (Figure 7) for [bmim][BF₄]. For latter our estimate by the FT-EOS is: $P = 20,6$ MPa. de Azevedo et al. [18] have reported the mild decrease of $\alpha_p(T)$ -dependence and the sharp decrease $\alpha_p(P)$ -dependence while a presumable cross-point is located between about 100 and 120 MPa for [bmim][BF₄]. Taking into account the above distinction in the evaluated (α_p, P, T) -surface it is interesting to consider their consequences for

TABLE 5: Comparison of excluded volumes (M/ρ^* [14] and b_0), characteristic interaction energy (ϵ^* [14] and $\bar{\epsilon}$), and effective number of bonded units ($MP^*/RT^*\rho^*$ [14, 15] and $\bar{N}_l$) (see text).

Compound	M/ρ^* (cm ³ /mol)	b_0 (cm ³ /mol)	ϵ^* (J/mol)	$\bar{\epsilon}$ (J/mol)	$MP^*/RT^*\rho^*$	$\bar{N}_l$
[bmim][BF ₄]	175,3	178	5642	2661	17,6	17,0
[bmim][PF ₆]	196,2	195,3	5658	2661	18,8	18,1

TABLE 6: Comparison of internal pressure $(\partial e/\partial v)_T$ for [bmim][BF₄] based on the LF-EOS [14] and FT-EOS (this work) with the values estimated [16] by experimental data on speed of sound W , density ρ , and isobaric heat capacity C_p .

T [14] (K)	$(\partial e/\partial v)_T$ (MPa)	T [16] (K)	$(\partial e/\partial v)_T'$ (MPa)	T [FT] (K)	$(\partial e/\partial v)_T$ (MPa)	ϵ_{coh} (J/cm ³)
313,1	482,78	283,15	459,91	290	743,76	555,15
332,6	471,50	288,15	459,31	310	573,16	486,41
352,6	460,35	293,15	459,20	330	463,91	437,85
372,7	450,11	298,15	457,79	350	388,61	401,57
392,8	440,00	303,15	455,76	370	333,84	373,35
412,9	429,23	308,15	453,73	390	292,27	350,67
432,6	419,35	313,15	451,20	410	259,66	331,94
452,3	408,84	318,15	448,06	430	233,40	316,13
472,2	399,19	323,15	446,64	450	211,77	302,52
		328,15	444,61	470	193,64	290,60
		333,15	443,09	490	178,19	280,01
		338,15	441,68	510	166,76	270,46
		343,15	439,75	517	162,41	267,31

caloric (C_v, P, T)-(C_p, P, T)- and C_v/C_p -surfaces shown in Figures 10–12.

The remarkable qualitative and even quantitative (<8%) correspondence between the predicted by FT-EOS C_v -values and those reported by de Azevedo et al. [18] follows from Figure 10. At the same time, although the discrepancies between C_p -values [18] and those predicted by the FT-EOS are again within acceptable limits (<10%) the formers demonstrate the weak maximum and very small pressure dependence for [bmim][BF₄] (for [bmim][PF₆] this $C_p(P)$ -dependence is monotonous as well as that predicted by the FT-EOS). It seems that the resultant ratio of heat capacity C_p/C_v shown in Figure 12 which demonstrates the irregular crossing of isotherms [18] is questionable. It suggests that their pressure dependence either needs the more accurate approximation or reflects the realistic distinction of reference FT-EOS from the actual behavior of [bmim][BF₄].

The lock of noticeable variations in pressure is the common feature of integration methodology [18] based on the given (W, P, T) - and (ρ, P, T) -surfaces. The unavoidable accumulation of uncertainties at each stage of calculations in the set $W - C_p - C_v$ may cause the unplausible behavior of adiabatic exponent C_p/C_v in liquid. The same is true for the set $C_v - C_p - W$ used in the FT-methodology. It is the most appropriate explanation of significant discrepancies for $W(P)$ -dependence shown in Figure 13. Let us remind also that the precise mechanical measurements of speed velocity [18] in the very viscous IL cannot be attributed exactly to the condition of constant entropy.

Thus, strictly speaking, the measured (W, P, T) -surface reflects the strong dispersive properties of media and must be less than its thermodynamic counterpart in the ideal (without a viscosity) liquid.

5. Conclusions

There are the structure-forming factors related to the above-discussed thermodynamic characteristic. Despite the certain discrepancies between the predicted and derived properties for FT-EOS and LF-EOS, both ones provide the close estimates of structure factors represented in Table 5.

Our aim here is to show that the thermodynamically-consistent predictions of thermodynamical properties by the FT-EOS yields also the molecular-based parameters which are, at least, realistic (see also Table 3). The estimate of average T -dependent well-depth $\bar{\epsilon}$ by (6b) as well as estimate of average value $\bar{N}_l$ by (24a) is related to the middle of temperature range: $T = 320$ K. The distinction of $\bar{\epsilon}$ from the respective ϵ^* -parameters of LF-EOS [14] can be attributed to the difference between nonbonded interactions in the discrete (LF-EOS) and continuum (FT-EOS) models of fluid. Our estimate of cohesive-energy density ϵ_{coh} by equality,

$$\epsilon_{\text{coh}} = \rho^2 (P_0, T) a(T) + \rho_l(T) r_\sigma(T), \quad (43)$$

represented in Table 6 seems also physically plausible. Maginn et al. [5, 6] have determined it within the framework of GEMC-simulations by the knowledge of $\rho(P_0, T)$ and

the internal energy difference between an ideal-gas ion pair and the average internal energy of an ion pair in the liquid state.

Such definition indicates that cohesive energy densities of many ILs are on the order of 500–550 J/cm³ (see, for comparison, Table 6) and demonstrate a slight decrease as temperature increases.

Another relevant characteristic is the internal pressure determined by the derivative of molar (or specific) internal energy,

$$\left(\frac{\partial e}{\partial v}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_\rho - P = T \frac{\alpha_P}{\beta_T} - P, \quad (44)$$

which is compared to ones calculated by different authors [14, 16] for [bmim][BF₄] in Table 6. As in the other cases, the FT-EOS predicts the much faster change of both cohesive energy density ε_{coh} and internal pressure $(\partial e/\partial v)_T$ as temperature increases.

One should collect a large number of precise experimental measurements to reconstruct the thermodynamic surface of a substance. FT-methodology provides a possibility of preliminary reliable estimates of relevant macroscopic and molecular-based correlations. Its thermodynamic consistency provides the serious advantage in comparison with the purely empiric treatment of any volumetric measurements at the description of derived heat capacities.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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